Cavity-Enhanced Measurements of Benzene for Environmental Monitoring

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Abstract: A laser sensor is developed for trace detection of benzene. It is based on a DFB-ICL near 3.3 µm and off-axis cavity-enhanced absorption, enabling minimum detection of 2 ppb for 6-second integration at room conditions.

OCIS codes: (010.1120) Air pollution monitoring; (280.3420) Laser sensors; (280.4788) Optical sensing and sensors

1. Introduction

Benzene (C_6H_6) is found in air from various emission sources, such as gasoline service stations, vehicle exhaust, coal/oil burning, and leaks in petroleum production processes. The World Health Organization (WHO) categorizes benzene as '*a major public health concern*' [1]. Fatal diseases such as cancer and aplastic anemia have been linked to human exposure to benzene. It is very important to have reliable, accurate and sensitive diagnostic methods and sensors for benzene detection at various facilities where benzene emissions are likely. There is, therefore, a huge demand for new and improved benzene sensors as the commercial ones lack in many respects. In this paper, we report the use of a mid-IR laser and cavity-enhanced absorption spectroscopy (CEAS) to develop a sensor for measuring trace amounts of benzene in practical environments where ethylene, methane and water vapor pose spectral interference challenges.

2. Sensor Description

Although benzene has absorption bands in the ultraviolet (UV) wavelength region, the broad features of most hydrocarbons in this region do not permit interference-free selective measurements. The infrared absorption spectrum, on the other hand, provides opportunities for highly selective detection of benzene and other pollutants. Based on the IR spectrum of benzene in the PNNL database [2], the best frequency to measure benzene is near 674 cm^{-1} (14.837 µm); however, this wavelength region is currently outside the range of commercially available semiconductor laser technology. In a previous work [3], low amounts of benzene were measured near 9.6 µm using a quantum-cascade laser. However, the selected wavelength (1038 cm^{-1}) had spectral interference from ozone which can be a challenge in many geographical locations. In another recent work [4], trace benzene concentrations were measured near 3.4 µm (3090 cm^{-1}) but isoprene interference was neglected whose concentration, and thus absorbance, might exceed that of benzene at various locations. Therefore, in this work, we have selected the ro-vibrational feature of benzene near 3.3 µm (3040 cm^{-1}) which has negligible ozone and isoprene interference. Although this region has spectral interference from ethylene, methane and water vapor [5], we implemented a multi-dimensional linear regression (MLR) algorithm and wavelength-scanning to measure the concentration of each of these species simultaneously.

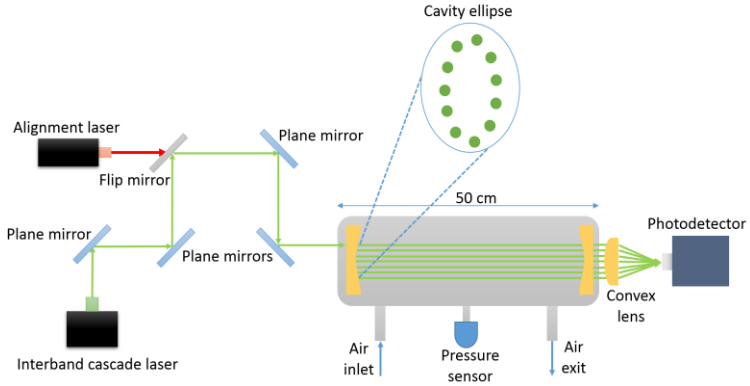

Fig. 1. Optical Schematic of the benzene sensor

An optical layout of the sensor designed in this work is shown in Fig. 1. The sensor uses a DFB interband cascade laser (DFB-ICL, Nanoplus) emitting near 3.3 µm with an output power ~ 1 – 2 mW. A Thorlabs 670 nm red laser was propagated collinearly with the IR laser to facilitate optical alignment. Two ZnSe mirrors of 99.97% nominal reflectivity (LohnStar Optics) were used to form a cavity in a 50 cm sampling cell. The laser was aligned in an off-axis cavity which suppressed the spurious coupling noise significantly compared to the on-axis cavity. The high mirror reflectivity, along with the low laser power, made the alignment and measurement very challenging as the transmitted laser intensity is very weak. The transmitted signal was collected *via* a focusing lens on to an AC-coupled, TE-cooled photodetector (bandwidth of 1.5 MHz, Vigo Systems).

3. Experimental Results

The mirror reflectivity specified by mirror manufacturers can have high uncertainty. Therefore, it is important to verify the reflectivity and, thereby, increase the measurement accuracy. Experiments were performed with known mixtures of C_6H_6/N_2 and the measured CEAS absorbance was compared with single-pass simulated absorbance. The mirror reflectivity was then calculated using $R = 1 - \frac{A_{sp}}{e^{A_{CEAS}-1}} = 99.96 \pm 0.024$ %, which results in an increase of ~ 3 orders of magnitude in absorbance compared to a single-pass arrangement. Benzene detection limit was found to be 200 ppt by extrapolating the measured data (see Fig. 2) to a minimum detectable absorbance of 0.1%. Thereafter, gas samples with known concentrations of benzene, ethylene, methane and water vapor were prepared to verify the diagnostic to measure benzene and interfering species simultaneously, which increased the minimum detection limit of benzene to 2 ppb. Finally, real air samples were collected from various locations and measured with the laser sensor as well as a gas chromatograph (GC), as shown in Fig. 3. Laser sensor based simultaneous measurements of benzene, ethylene, methane and water vapor are listed in Table 1. As expected, the benzene concentration was highest at the gas station.

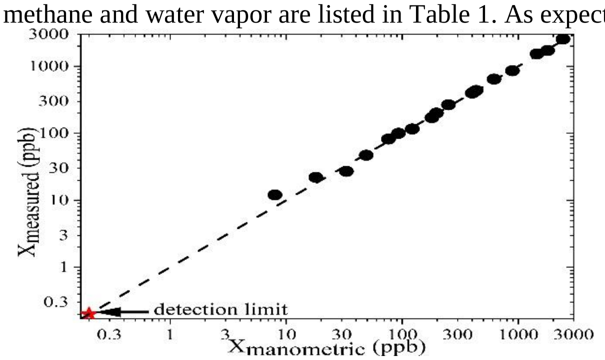

Fig. 2. Measured benzene mole fraction versus benzene mole fraction calculated manometrically

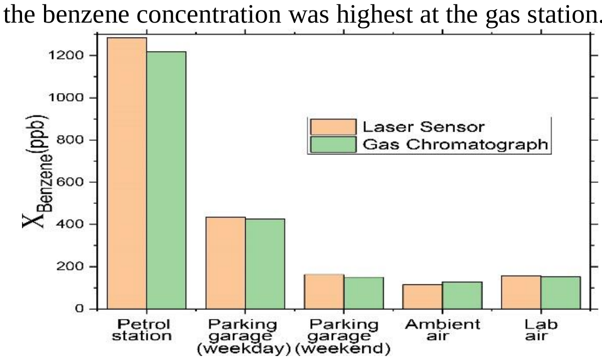

Fig. 3. Comparison between the benzene concentration measured by the laser sensor and gas chromatograph

Table 1: Measured concentrations of benzene, ethylene, methane and water vapor in the collected samples

Sample	Benzene (ppb)	Ethylene (ppb)	Methane (ppb)	Water Vapor (%)
Petrol station	1217	1872	991	1.1
Parking garage (weekday)	425	597	882	0.81
Parking garage (weekend)	150	697	350	1
Ambient air	128	589	287	1.17
Laboratory air	152	796	1198	1.29

4. Conclusions

A laser sensor based on cavity enhanced absorption spectroscopy has been developed to measure trace concentrations of benzene. The single pass absorption increased by three orders of magnitude due to the high reflectivity of the mirrors, thus enabling benzene detection down to 2 ppb in the presence of interfering species. The sensor was validated with a gas chromatograph, and can simultaneously measure benzene, ethylene, methane and water vapor. The sensor can be applied to monitor air quality in petrochemical facilities where the emissions of these species are likely.

4. Acknowledgement

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5. References

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